

Performance of colloidal silica and ceria based slurries on CMP of Si-face 6H-SiC substrates



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ABSTRACT

Colloidal silica and ceria based slurries, both using KMnO_4 as an oxidizer, for chemical mechanical polishing (CMP) of Si-face (0001) 6H-SiC substrate, were investigated to obtain higher material removal rate (MRR) and ultra-smooth surface. The results indicate that there was a significant difference in the CMP performance of 6H-SiC between silica and ceria based slurries. For the ceria based slurries, a higher MRR was obtained, especially in strong acid KMnO_4 environment, and the maximum MRR (1089 nm/h) and a smoother surface with an average roughness R_a of 0.11 nm was achieved using slurries containing 2 wt% colloidal ceria, 0.05 M KMnO_4 at pH 2. In contrast, due to the attraction between negative charged silica particles and positive charged SiC surface below pH 5, the maximum MRR of silica based slurry was only 185 nm/h with surface roughness R_a of 0.254 nm using slurries containing 6 wt% colloidal silica, 0.05 M KMnO_4 at pH 6. The polishing mechanism was discussed based on the zeta potential measurements of the abrasives and the X-ray photoelectron spectroscopy (XPS) analysis of the polished SiC surfaces.

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1. Introduction

Due to its outstanding properties, such as wide band gap, good thermal conductivity, high heat resistance, high temperature stability and good crystal lattice arrangement with GaN, silicon carbide (SiC) has become a promising semiconductor material for high power and high frequency electric applications [1–3]. Many of these applications require a flat and defect-free SiC substrate surface; however, it is difficult to obtain high removal rates because of its high mechanical hardness and strong chemical inertness [4].

Chemical mechanical polishing (CMP) is one of the most effective ways to produce ultra-smooth undamaged surfaces in semiconductor industry. Currently, several researchers have studied the CMP of SiC single crystal substrates using colloidal silica with different chemicals [5–8]. The material removal rate (MRR) and surface quality varied greatly with the different crystal face orientations during the CMP of 6H-SiC single crystal substrates and a maximum in material removal rate (MRR) was measured for the Si-face of 153 nm/h with an average RMS roughness of 0.096 nm using colloidal silica in KOH solution [5]. A mixed abrasive slurry containing colloidal silica and nano-diamond at high pH value was used in the CMP of 6H-SiC substrates and the MRR and R_a were

153 nm/h and 0.27 nm, respectively [7]. Fe nanoparticles, as well as Pt/C nanoparticles were used as a catalyst added into the colloidal silica based slurry, and the MRR of 120 nm/h and R_a of 0.05 nm were achieved for Si-face 4H-SiC wafer [8]. However, the MRR of these experiments were not high enough for industry applications. In order to shorten the CMP process, it is necessary to investigate a highly efficient CMP slurry for SiC single crystal substrates.

A CMP process could be significantly influenced by many factors, such as abrasives, pH value, oxidants, etc. Among the various oxidants, KMnO_4 is a strong oxidizer and it can etch the SiC without friction [9]. Furthermore, ceria abrasives have been reported to have high chemical reactivity and can increase removal rate in Silica polishing [10]. However, little effort has been made to investigate the slurries containing potassium permanganate with silica or ceria for CMP of SiC substrates. In this paper, the CMP performance of Si-face (0001) 6H-SiC single crystal substrates were compared between silica and ceria based slurries, both using KMnO_4 as an oxidizer. The zeta potentials of silica and ceria particles in the presence of KMnO_4 were investigated and the chemical composition of the polished surfaces was studied using X-ray photoelectron spectroscopy (XPS). The polishing mechanism of the SiC substrates was also discussed.

2. Materials and experimental methods

N-type, 2-inch diameter Si-face (0001) 6H-SiC single crystal wafers (TanKeBlue Semiconductor Co. Ltd, Beijing, China) were

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Table 1
CMP process conditions.

	Parameters
Substrate	Si-face 6H-SiC, 2-inch
Polisher	CETR CP-4
Conditioning	Ex situ
Pad	IC-1000 (K-Groove)
Pressure	4 psi
Slurry flow rate	90 ml/min
Platen/carrier speed	90/90 rpm
Polishing time	20 min

used in the polishing experiments. Silica abrasives (Nexsil 85A, mean diameter of 50 nm, 30 wt% acid-stabilized colloidal aqueous, Nyacol Nano Technologies) and ceria abrasives (Tizox 9872, mean diameter of 140 nm, 50 wt% colloidal aqueous, Ferro Corp.) were diluted to use at different particle concentration. The chemical additives, potassium permanganate (KMnO_4 , $\geq 99\%$), nitric acid (aq. HNO_3 , 70%), and potassium hydroxide (KOH , $\geq 85\%$) were obtained from Sigma–Aldrich Corporation and used without further purification.

The slurries were prepared by dissolving the chemical additives in deionized water followed by adding abrasives to this solution, then stirred using a magnetic stirrer for about 10 min. The effect of pH value, abrasive and KMnO_4 concentration on the MRR of 6H-SiC were investigated through orthogonal test in our previous work. The results show that the pH value is the most important factor. Therefore, in this paper, the concentration of silica particles, ceria particles and KMnO_4 were kept at 6 wt%, 2 wt% and 0.05 M, respectively.

The CMP experiment was performed on CETR CP-4 polisher using a polyurethane IC-1000 K-Groove pad supplied by Dow Electronic Materials (Newark, DE). The polishing pad was conditioned (ex situ) by a 4-inch diamond grit conditioner (3M, Inc.). Each CMP experiment was done for a duration of 20 min at 4 psi down pressure with the slurry flow rate of 90 ml/min and the platen/carrier speed of 90/90 rpm (Table 1). All the 6H-SiC wafers were pre-polished with slurries only containing 6 wt% colloidal silica at pH 8 and each CMP experiment was repeated three times.

The MRR was calculated by measuring the weight loss of the wafer before and after polishing using an electronic balance with the accuracy 0.01 mg (Mettler Toledo AG 285) and expressed in nm/h. The surface morphology of the wafer was measured using an atomic force microscope (AFM). The zeta potentials of silica and ceria particles in the presence of KMnO_4 at different pH values (adjusted with KOH or HNO_3) were determined at room temperature using a zeta plus particle apparatus (Nano-ZS, Malvern). XPS experiments were carried out on a RBD upgraded PHI-5000C ESCA system (PerkinElmer) with Mg $K\alpha$ radiation ($h\nu = 1253.6$ eV) or Al $K\alpha$ radiation ($h\nu = 1486.6$ eV). The X-ray anode was run at 250 W, the high voltage was kept at 14.0 kV with a detection angle at 54° and the base pressure of the analyzer chamber was around 5×10^{-8} Pa.

3. Results and discussion

3.1. CMP of Si-face 6H-SiC

Fig. 1 shows the effect of pH value ranging from 4 to 10 on the MRR of 6H-SiC using silica based slurries. The MRR increased with the increase of pH value in the beginning. After it reached the maximum of 185 nm/h at pH 6, then MRR decreased with the increase of pH value. While the MRR decreased sharply with the increase of pH value ranging from 2 to 8 in ceria based slurries, as shown in Fig. 2. The maximum of MRR was 1089 nm/h at pH 2.

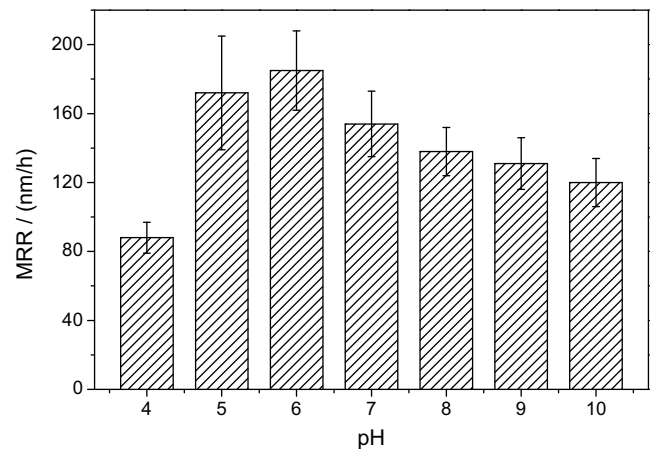


Fig. 1. The effect of pH value on the MRR of 6H-SiC with silica based slurries.

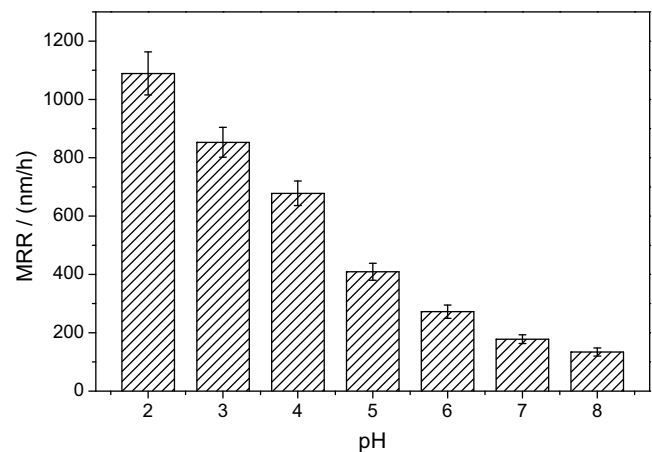


Fig. 2. The effect of pH value on the MRR of 6H-SiC with ceria based slurries.

Fig. 3 shows the surface morphology of 6H-SiC polished by the silica based slurry at pH 6. It can be seen that the post-polished surface of Si-face 6H-SiC was excellent with an average roughness R_a of 0.25 nm. A smoother surface with an average roughness R_a of 0.11 nm can be achieved using the ceria based slurry at pH 2, as shown in Fig. 4. The better surface quality may be due to the fact that the mohs' hardness of ceria is lower than that of silica.

3.2. Zeta potential of ceria and silica particles

The electrostatic interactions between abrasive particles and wafer surface are the cause for the particle adhesion to the wafer surface, this may cause particle contamination of the wafer surface and reduce the contact area between the wafer surface and oxidant, suppressing the material removal in the CMP of SiC. In order to study these electrostatic interactions in our CMP process, the zeta potentials of silica and ceria particles in the presence of KMnO_4 were investigated in the pH range from 2 to 10. Both the zeta potentials of silica and ceria particles decreased with the increasing of pH values, as shown in Fig. 5. Silica particles were negatively charged in the entire pH range, while ceria particles were positive charged over the pH range of 2–8 and its isoelectric point was around pH 8, similar to the results reported by Veera Dantu et al. [11].

The iso-electric point (IEP) of SiC in DI water is about 5 [12]. Therefore, positive charged SiC surface was expected to be repelled by ceria particles for the pH values from 2 to 5 and be attracted from 5 to 8. In contrast, negative charged silica particles were expected

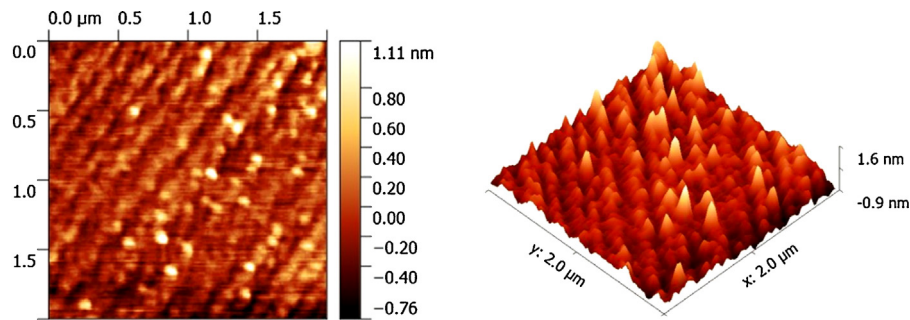


Fig. 3. The AFM surface morphology of 6H-SiC polished with 6 wt% SiO_2 + 0.05 M KMnO_4 at pH 6.

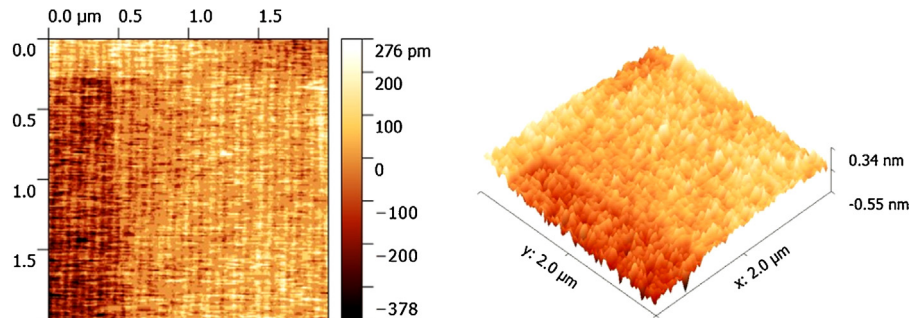


Fig. 4. The AFM surface morphology of 6H-SiC polished with 2 wt% CeO_2 + 0.05 M KMnO_4 at pH 2.

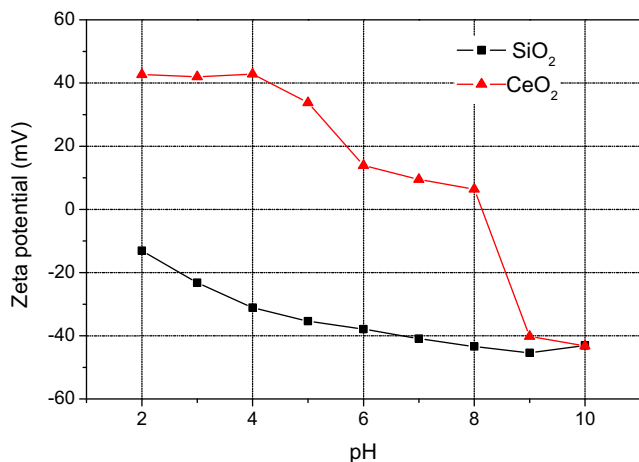


Fig. 5. The zeta potentials of silica and ceria particles in the presence of KMnO_4 .

to be attracted by positive charged SiC surface below pH 5, which might reduce the oxidation area of the SiC surface.

3.3. XPS analysis of 6H-SiC polished surfaces

Peaks corresponding to the C 1s, O 1s, Si 2s and Si 2p photoelectrons are clearly seen in the XPS survey scan spectra of the polished 6H-SiC surfaces, as shown in Fig. 6. The spectra of the polished surface were similar except for a shorter O 1s peak in the presence of KMnO_4 .

Table 2 shows the atomic compositions (%) of the 6H-SiC surfaces polished with different slurries. From the data illustrated in Table 2, it can be seen that the surface concentration of oxygen in the pre-polished 6H-SiC surfaces could be reduced in the CMP process using slurries containing KMnO_4 . And the C/Si ratio was higher in the polished SiC surfaces than in the pre-polished SiC surfaces, especially when ceria particles were used, indicating that Si was removed faster than C during the CMP process. Furthermore, the

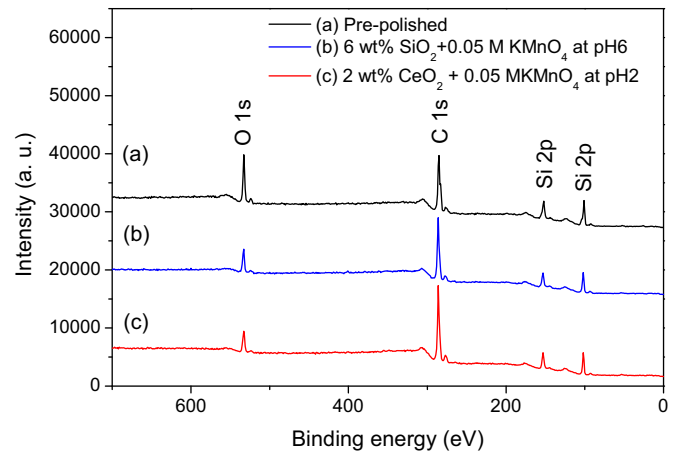


Fig. 6. XPS survey scans of the 6H-SiC surfaces: (a) pre-polished, (b) polished with 6 wt% SiO_2 + 0.05 M KMnO_4 at pH 6, (c) polished with 2 wt% CeO_2 + 0.05 M KMnO_4 at pH 2.

Table 2

Atomic concentrations (%) of the 6H-SiC surfaces.

	C 1s	O 1s	Si 2p	C/Si	O/Si
Pre-polished	57.8	18.2	23.9	2.4	0.8
6 wt% SiO_2 + 0.05 M KMnO_4 at pH 6	66.4	11.5	21.3	3.1	0.5
2 wt% CeO_2 + 0.05 M KMnO_4 at pH 2	69.7	10.3	19.9	3.5	0.5

C/Si ratio of the polished surfaces was significantly higher than the normal stoichiometric value of 1.

Fig. 7 demonstrates the Si 2p and C 1s spectra of the Si-face 6H-SiC surfaces polished with different slurries. There were three main peaks due to Si–C (100.4 eV), Si–C–O (101.1 eV) and SiO_xC_y (101.9) on the Si-face 6H-SiC surfaces polished with different slurries, as shown in Si 2p curve-fitting result of Fig. 7(a, c, e) [13,14]. The chemical state of carbon atoms was also analyzed using C 1s spectra of the Si-face 6H-SiC surfaces polished with different slurries, as shown in

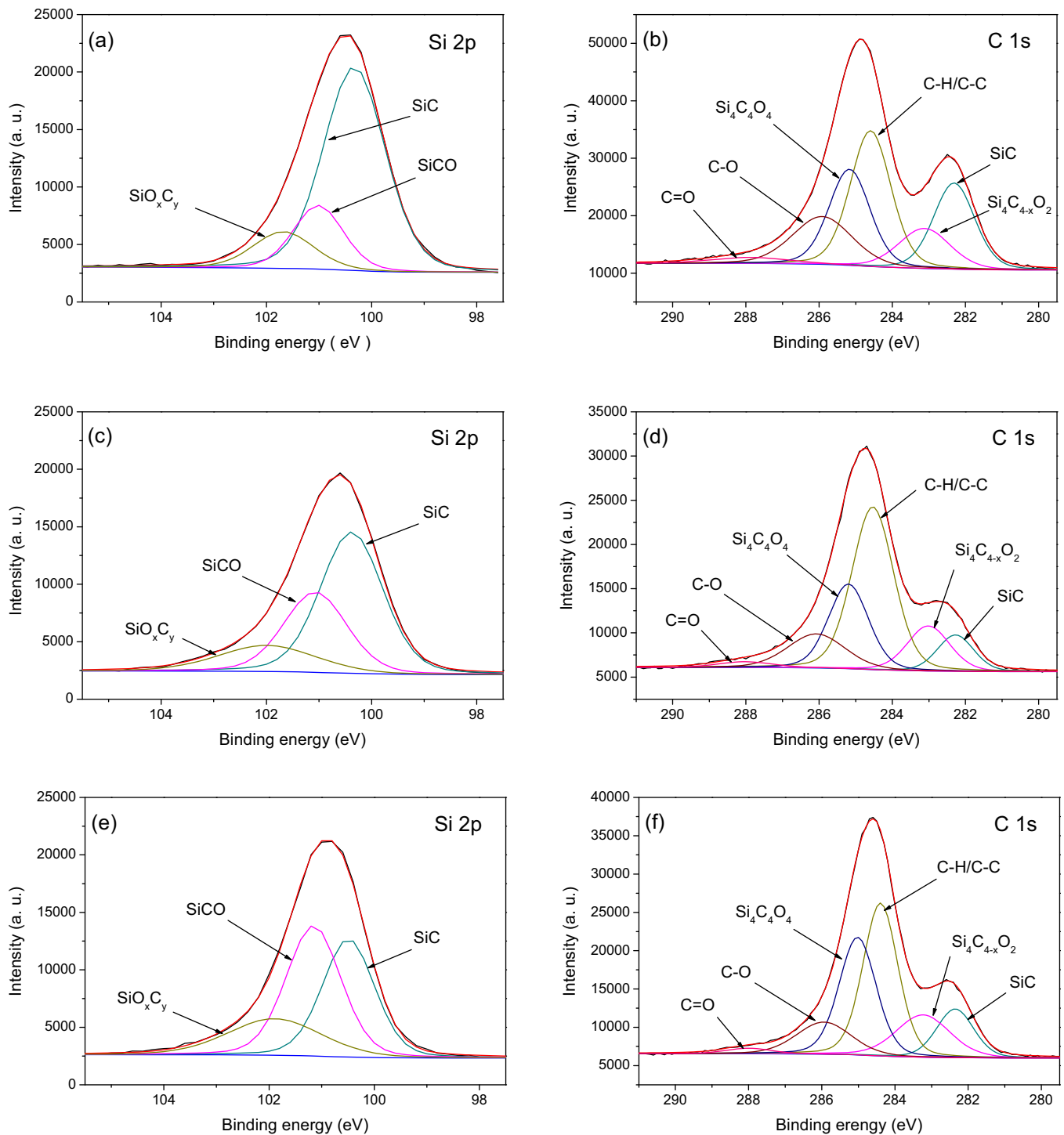


Fig. 7. Si 2p and C 1s spectra of the Si-face 6H-SiC surfaces: (a, b) pre-polished; (c, d) polished with 6 wt% SiO₂ + 0.05 M KMnO₄ at pH 6; (e, f) polished with 2 wt% CeO₂ + 0.05 M KMnO₄ at pH 2.

Fig. 7(b, d, f). Six peaks near 282.4 eV, 283.2 eV, 284.6 eV, 285.1 eV, 286.1 eV, 288 eV, corresponding to C 1s of SiC, Si₄C_{4-x}O₂, C–C/C–H, Si₄C₄O₄, C–O and C=O binding energy, respectively [15,16], were observed in C 1s curve-fitting results. The peaks of C–C/C–H were generally detected in C 1s spectra, resulted from the contamination of the carbon in ambient or adhesive component of the polishing surface [17], leading to the unmoral of the C/Si ratio on the SiC surface demonstrated in Table 2. As can be seen in Fig. 7, the concentrations of the oxidized species, such as Si–C–O, SiO_xC_y, Si₄C_{4-x}O₂, Si₄C₄O₄, C–O and C=O, were significantly higher in the SiC surfaces

polished with slurries containing KMnO₄ than in the pre-polished SiC surface. The peak near 100.4 eV and 282.4 eV, corresponding to Si 2p and C 1s of SiC binding energy, respectively, decreased dramatically in the 6H-SiC surface polished with slurries containing KMnO₄, especially at pH 2.

The relative proportions of the chemical components on the SiC surfaces are listed in Table 3. From the data revealed in Table 3, it can be seen clearly that the relative atomic concentration of Si–C in Si 2p spectra was lower in the SiC surfaces polished with slurries containing KMnO₄ than in the pre-polished SiC surface. The proportion

Table 3

The atomic concentration of different chemical components at 6H-SiC surfaces.

		Pre-polished	6 wt% SiO ₂ + 0.05 M KMnO ₄ at pH 6	2 wt% CeO ₂ + 0.05 M KMnO ₄ at pH 2
Si 2p	Si—C	69.9	53.8	36.9
	Si—C—O	17.7	30.8	42.7
	Si—O _x —C _y	12.4	15.4	20.4
C 1s	Si—C	27.5	14.8	17.3
	Si ₄ C _{4-x} O ₂	16.0	21.6	21.9
	Si ₄ C ₄ O ₄	30.6	38.1	41.7
	C—O	22.2	22	16.7
	C=O	3.6	3.6	2.4

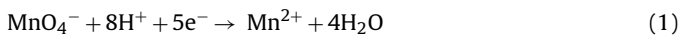
of oxidized species of Si—C, such as Si—C—O and SiO_xC_y, increased in the SiC surfaces polished with slurries containing KMnO₄, indicating that the oxidation happened on the SiC surfaces. Furthermore, a similar result can be found in C 1s spectra of 6H-SiC surface. However, the silicon-free carbonaceous species, such as C—O and C=O, which are not bonded to any silicon atom and hard to remove from the surface [18], was lower in the SiC surface polished by ceria-based slurry at pH 2 than by silica-based slurry at pH 6.

3.4. Polishing mechanism

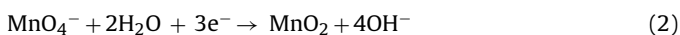
There are two key steps involved in the SiC CMP removal mechanism: an oxide layer is formed on the surface of SiC substrates by oxidation and then removed by mechanical abrasion.

In the CMP process, atoms on the SiC surface were oxidized by KMnO₄ (as shown in Table 3) and the oxidized species of Si—C (e.g. Si_xC_yO_z or SiO_xC_y) could be further oxidized or hydrolyzed to form carbon-free silicon oxide species [18], then removed by mechanical abrasion.

The oxidizing strength of KMnO₄ decreases with the increase of pH value. In the acidic pH range, KMnO₄ acts as a strong oxidizer and can be reduced to Mn²⁺ via the following reaction:



While in the near neutral pH region, KMnO₄ can be reduced to MnO₂ via the following reaction:



And in the alkaline pH range, KMnO₄ can be reduced to MnO₄²⁻ via the following reaction:



Based on the XPS analysis and the properties of KMnO₄, it can be seen that the increase of the atomic compositions of the oxidized species of Si—C (e.g. Si_xC_yO_z or SiO_xC_y) and the decrease of silicon-free carbonaceous species (e.g. C—O and C=O) may be attributed to the strong oxidizing ability of KMnO₄ in low pH values. In other words, the silicon-free carbonaceous species may be further oxidized to organic acid, carbon oxide or carbon dioxide in strong acid aq. KMnO₄.

However, negative charged silica particles can be attracted by positive charged SiC surface below pH 5 (as shown in Fig. 5), inhibiting the material removal in the CMP of SiC.

In addition, ceria particles are reported to have a chemical tooth property. During the CMP of SiC, Si—O—Ce bonds can be formed between ceria particles and the oxide layer, then removed rapidly by the mechanical abrasion force [19]. Due to the physical and chemical reaction of the ceria, a higher MRR of the SiC CMP is obtained, especially in strong acid KMnO₄ environment.

4. Conclusions

In this paper, the CMP performance of Si-face (0001) 6H-SiC substrates were compared between silica and ceria based slurries, both using KMnO₄ as an oxidizer. The maximum MRR (1089 nm/h) and a smoother surface with an average roughness Ra of 0.11 nm was achieved using slurries containing 2 wt% colloidal ceria, 0.05 M KMnO₄ at pH 2. In contrast, the maximum MRR of silica based slurry was only 185 nm/h with surface roughness Ra of 0.254 nm using slurries containing 6 wt% colloidal silica, 0.05 M KMnO₄ at pH 6. On the basis of zeta potential measurements, silica particles were negatively charged in the entire pH range from 2 to 10, resulting in the attraction between negative charged silica particles and positive charged SiC surface below pH 5. While ceria particles were positive charged over the pH range of 2–8. XPS analysis of the polished SiC surface showed that the C/Si ratio was higher in the polished SiC surfaces than in the pre-polished SiC surfaces, especially when ceria particles were used at pH 2, indicating that Si was removed faster than C during the CMP process.

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References

- [1] Y.C. Lin, C.H. Kao, A study on surface polishing of SiC with tribochemical reaction mechanism, *Int. J. Adv. Manuf. Technol.* 25 (1–2) (2005) 33–40.
- [2] D. Fan, A study on the polishing mechanism of silicon carbide (SiC) optic surface, *Adv. Mater. Res.* 337 (2011) 474–478.
- [3] X.F. Chen, J. Li, D.Y. Ma, Fine machining of large-diameter 6H-SiC wafer, *J. Mater. Sci. Technol.* 22 (5) (2006) 681–684.
- [4] H. Nitta, A. Isobe, P.J. Hong, et al., Research on reaction method of high removal rate chemical mechanical polishing slurry for 4H-SiC substrate, *Jpn. J. Appl. Phys.* 50 (2011) 046501.
- [5] X.F. Chen, X.G. Xu, X.B. Hu, et al., Anisotropy of chemical mechanical polishing in silicon carbide substrates, *Mater. Sci. Eng. B* 142 (1) (2007) 28–30.
- [6] X.L. Shi, G.S. Pan, Y. Zhou, et al., Characterization of colloidal silica abrasives with different sizes and their chemical-mechanical polishing performance on 4H-SiC (0001), *Appl. Surf. Sci.* 307 (2014) 414–427.
- [7] H. Lee, B. Park, S. Jeong, et al., The effect of mixed abrasive slurry on CMP of 6H-SiC substrates, *J. Ceram. Process. Res.* 10 (3) (2009) 378–381.
- [8] Y. Zhou, G.S. Pan, X.L. Shi, et al., Chemical mechanical planarization (CMP) of on-axis Si-face wafer using catalyst nanoparticles in slurry, *Surf. Coat. Technol.* 251 (2014) 48–55.
- [9] Z.Z. Zhu, V. Muratov, T.E. Fischer, Tribochemical polishing of silicon carbide in oxidant solution, *Wear* 225–229 (2) (1999) 848–856.
- [10] L.Y. Wang, K.L. Zhang, Z.T. Song, et al., Ceria concentration effect on chemical mechanical polishing of optical glass, *Appl. Surf. Sci.* 253 (2007) 4951–4954.
- [11] P.R. Veera Dandu, V.K. Devarapalli, S.V. Babu, Reverse selectivity-high silicon nitride and low silicon dioxide removal rates using ceria abrasive-based dispersions, *J. Colloid Interface Sci.* 347 (2010) 267–276.
- [12] B.P. Singh, J. Jena, L. Besra, et al., Dispersion of nano-silicon carbide (SiC) powder in aqueous suspensions, *J. Nanopart. Res.* 9 (2007) 797–806.
- [13] R. Michel, A. Ahmed, S. Karin, et al., Covalent attachment of organic monolayers to silicon carbide surfaces, *Langmuir* 24 (2008) 4007–4012.
- [14] X.A. Fu, C.A. Zorman, M. Mehregany, Chemical mechanical polishing of cubic silicon carbide films grown on Si (100) wafers, *J. Electrochem. Soc.* 149 (12) (2002) G643–G647.
- [15] T. Maruyama, H.J. Bang, N. Fujita, et al., STM and XPS studies of early stages of carbon nanotube growth by surface decomposition of 6H-SiC (0001) under various oxygen pressures, *Diam. Relat. Mater.* 16 (2007) 1078–1081.
- [16] B. Hornetz, H.J. Michel, J. Halbritter, et al., ARXPS studies of SiO₂–SiC interfaces and oxidation of 6H SiC single crystal Si-(001) and C-(001) surfaces, *J. Mater. Res.* 9 (1994) 3088–3094.
- [17] K. Yamamura, T. Takiguchi, M. Ueda, et al., Plasma assisted polishing of single crystal SiC for obtaining atomically flat strain-free surface, *CIRP Ann.: Manuf. Technol.* 60 (2011) 571–574.
- [18] U.R.K. Lagudu, S. Isono, S. Krishnan, et al., Role of ionic strength in chemical mechanical polishing of silicon carbide using silica slurries, *Colloids Surf. A: Physicochem. Eng. Asp.* 445 (2014) 119–127.
- [19] T. Hoshino, Y. Kurata, Y. Terasaki, et al., Mechanism of polishing of SiO₂ films by CeO₂ particles, *J. Non-Cryst. Solids* 283 (2001) 129–136.